Synthesis, Structure and Reaction of {Tris[2-(dimethylamino)phenyl]germyl}lithium (SYNTHETIC ORGANIC CHEMISTRY-Synthetic Design)

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Atsushi Kawachi, Yoko Tanaka and Kohei Tamao

{Tris[2-(dimethylamino)phenyl]germyl}lithium (**1**) has been prepared from the corresponding hydrogermane (**3**) with *tert*-butyllithium. X-ray analysis of **1** shows that **1** exists as a mono-chelated monomer, where the lithium atom is coordinated with one of the amino groups and with two THF molecules. Reaction of **1** with elemental selenium gives 2,2,4,4-tetrakis[2-(dimethylamino)phenyl]-1,3,2,4-diselenadigermetane (**2**). The nitrogen donor induces a novel type of reaction for the formation of the heterocyclic compound.

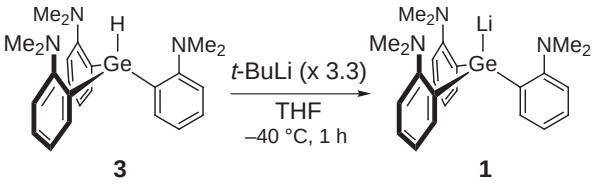
Keywords: Germyllithium / 2-(Dimethylamino)phenyl ligand / Chelation / Solid-state structure / Diselenadigermetane

Among a variety of Group 14 element-alkali metal compounds, germyllithium compounds have been well studied from the synthetic view point, but structural studies have been less developed. Thus germanium-lithium bond character is still unclear. We report here the preparation of {tris[2-(dimethylamino)-phenyl]germyl}lithium (**1**) and its structure in the solid state. We also report the reaction of **1** with elemental selenium to result in formation of 1,3,2,4-diselenadigermetane **2**.

1. Synthesis and Structure of 1 [1]

The germyllithium **1** was prepared by deprotonation of the hydrogermane **3** [2] with *tert*-butyllithium (3.3 mol amt.) in THF at –40 °C in 93% yield, as shown in Scheme 1; the yield was estimated by quenching with D_2O. When **3** was treated with a deficient amount of *tert*-butyllithium (1.2 mol amt.), **1** could be isolated as pale yellow crystals in 33% yield after recrystallization from toluene at –20 °C.

Scheme 1



3 **1**

X-ray analysis of the crystal reveals that **1** has a monomeric structure in the solid state, as shown in Figure 1. The most striking feature is the highly distorted geometry around Ge(1) due to the unsymmetrical interaction of Li(1) with the amino group. Li(1) bonded to Ge(1) is coordinated with N(1) of one of the three NMe_2 groups, forming a five-membered chelate ring consisting of Li(1), Ge(1), C(1), C(2), and N(1). Li(1) is also coor-

SYNTHETIC ORGANIC CHEMISTRY –Synthetic Design–

Scope of research

(1) Synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds, functionalized silyl anions, and functionalized oligosilanes. (2) Design and synthesis of novel π-conjugated polymers containing silacyclopentadiene (silole) rings, based on new cyclization reactions and carbon-carbon bond formations mediated by the main group and transition metals. (3) Chiral transformations and asymmetric synthesis via organosulfur and selenium compounds, especially via chiral episulfoniun and episelenonium ions.

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dinated with O(1) and O(2) of two THF molecules arising from the reaction solvent. The Li(1)–Ge(1) bond length (2.598(9) Å) is the shortest among those of the characterized germyllithium compounds (2.613(3)–2.759(24) Å). The Li(1)–N(1) bond length (2.15(1) Å) is longer than the sum of the covalent radii (Li 1.23 Å; N 0.70 Å), but normal as the coordinative Li–N bonds (2.01–2.17 Å). The intramolecular coordination of N(1) to Li(1) reduces the angle of Li(1)–Ge(1)–C(1) to 83.9(3)°. As a result, Li(1), Ge(1), C(9), and C(17) are almost coplanar; the sum of the three angles of Li(1)–Ge(1)–C(9), Li(1)–Ge(1)–C(17), and C(9)–Ge(1)–C(17) is 359.5°. In spite of the distorted geometry, however, there are no significant differences among the three Ge–C bonds (2.042(6), 2.030(5), and 2.054(5) Å) and the three C–Ge–C angles (96.8(2), 99.2(2), and 98.4(2)°). It is also noted that the sum of the latter (294.4°) is strongly reduced from the sp^3 tetrahedral value (328°). Thus, the geometry of **1** may be designated pyramidal rather than distorted tetrahedral.

We performed an *ab initio* calculation of **1**•$(THF)_2$ at HF level using the 6-311+G* basis set on Li and Ge atoms and the 6-31G basis set on H, C, N, and O atoms. The molecular orbital analysis of the anionic electrons (HOMO) indicates that the lithium atom is located not along the vector of the anionic electrons but aside. This may be represented as an intramolecular separated ion pair, which is not unusual if the Ge–Li interaction is weak while the N–Li coordinative interaction is relatively strong.

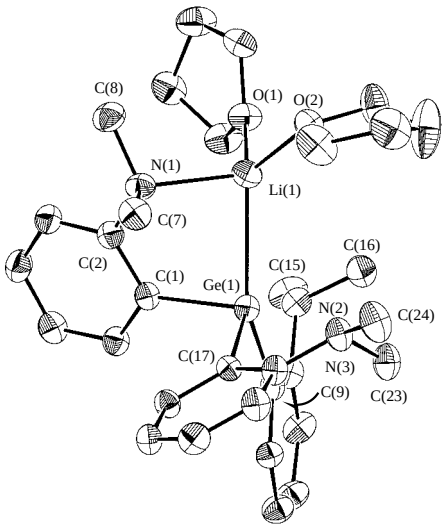
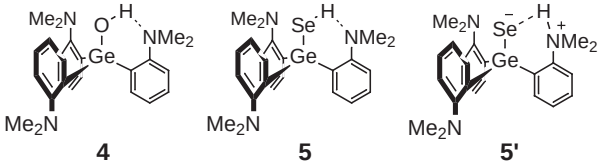


Figure 1. Molecular structure of **1**•$(THF)_2$ with 30% probability ellipsoids (H atoms omitted for clarity).

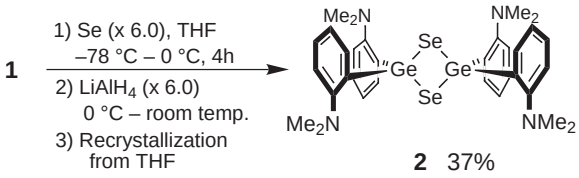
2. Reaction of 1 with Selenium [3]

Previously we reported the preparation and structure of tris[2-(dimethylamino)phenyl]germanol (**4**), which contains the germanium–oxygen bond and exhibits intramolecular hydrogen bonding between the hydroxyl group and one of the amino groups [2]. This finding prompted us to prepare and isolate a heavier Group 16 element analog, germaneselenol **5**.



The germyllithium **1** in THF was allowed to successively react with selenium powder and with lithium aluminum hydride, followed by hydrolysis. Crystallization of the product from THF did not afford **5** but unexpectedly afforded the diselenadigermetane **2** in 37 % yield, as shown in Scheme 2.

Scheme 2



The molecular structure of **2** was determined by X-ray analysis. The Ge–Se bond lengths are 2.3678(6) and 2.3716(9) Å, which are among the normal Ge–Se single bond lengths (2.337–2.421 Å). The intramolecular Ge···Ge distance is 3.168(1) Å. The ratio of the Ge···Ge nonbonding distance to the Ge–Se bond length is 1.34, which is in good agreement with the values of the approximate homology rule proposed by Kabe and Masamune [4].

The mechanism of the formation of **2** is still unclear, but **2** turned out to be the secondary product from the zwitterionic species **5'**, perhaps via intra- and/or intermolecular protodegermylation, as indicated by the ^1H NMR results. Thus the nitrogen donor intramolecularly activates the selenol proton, inducing a novel type of reaction for the formation of the heterocyclic compound.

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